



Phase III Final Technical Report A

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***Ultra-High Conductivity Umbilicals:
Polymer Nanotube Umbilicals (PNUs)***

10121-4302-01

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**Phase III Final Technical Report
NanoRidge Materials, Inc.
Contract Number 10121-4302-01**

Abstract

This final report a) summarizes briefly Phases I and II, b) describes the work performed in Phase III, and c) documents the achievements made during the year. The work performed was executed according to the Project Management Plan, while the team made best efforts to maintain the agreed schedule. The Phase III tasks included a) optimizing carbon nanotube (CNT) conductor, b) developing a continuous manufacturing process, and c) performing limited production. The achievements included 1) procurement and installation of a lab scale production furnace, 2) greatly improved fiber purity, and 3) development of a continuous production process. The stated goal (performance deliverable) was to “show evidence of a conductor with resistivity between 1×10^{-6} and $9 \times 10^{-6} \Omega \cdot \text{cm}$ capable of operating at a pressure from 34.47 to 37.92 MPa (5000 to 5500 psig).” An extended wire length was overjacketed and tested at 37.92 MPa. The resistance of the wire was measured as a function of pressure. The resistance fluctuated slightly over the pressure range 0 to 5504 psig. To perform the test, the CNT bare conductor was the product of a four hour production run, the conductor was overjacketed, the wire ends were stripped, and the jacketed wire was spliced into copper with silver paste and then potted. Also, described is a protocol that provided a wire with $6.7 \times 10^{-6} \Omega \cdot \text{cm}$ resistivity. Based on the project achievements of Phases I through III, NanoRidge Materials, Inc. highly recommend continuation of the development program.

TABLE OF CONTENTS

1.	EXECUTIVE SUMMARY	7
2.	REPORT DETAILS.....	8
2.1	PHASE I CONCLUSIONS	8
2.2	PHASE II CONCLUSIONS	9
2.3	PHASE III EXPERIMENTAL METHODS.....	10
2.3.1	SUBTASK 5.3.1.1 – PRODUCE OPTIMIZED CONDUCTOR.....	11
2.3.2	SUBTASK 5.3.1.1.1 (RICE 3.1) – MANIPULATION AT PRESSURE	12
2.3.3	SUBTASK 6.1.1.1 – DEVELOP CONTINUOUS PROCESS.....	13
2.3.4	SUBTASK 6.1.1.1.1 (RICE 3.2) – SUPPORT CONTINUOUS PROCESS	14
2.3.5	SUBTASK 6.1.1.2 – LIMITED PRODUCTION	16
2.3.6	SUBTASK 6.1.1.3 – TEST CONNECTIONS.....	16
2.3.7	SUBTASK 6.2.1.2 – TARGETED OPTIMIZATION	16
2.3.8	SUBTASK 6.2.1.2.1 (RICE 3.3) – EXCEED $10^{-6} \Omega \bullet \text{CM}$ RESISTIVITY	17
2.4	PHASE III RESULTS AND RECOMMENDATIONS	18
2.4.1	GROWTH OPTIMIZATION	18
2.4.2	CONTINUOUS PRODUCTION	20
2.4.3	WIRE CHARACTERIZATION AND PURIFICATION	21
2.4.4	ELECTRICAL AND PRESSURE TESTING RESULTS	25
2.5	CONCLUSIONS	28
2.6	RECOMMENDATIONS	28
3.	FIGURES AND TABLES	29
4.	REFERENCES.....	30
5.	LIST OF ACRONYMS AND ABBREVIATIONS.....	30

1. EXECUTIVE SUMMARY

The Research Partnership to Secure Energy for America (RPSEA) contract, 10121-4302-01, was a three year and three month, \$3.4 M phased project with NanoRidge Materials, Inc. as the Prime Subcontractor. Thus far, additional technical participants include subcontractors Rice University, Cambridge University, and Technip Umbilicals. Rice University is the largest subcontracted participant, while Technip Umbilicals began to contribute in Phase II. Cambridge University was a key contributor in Phase I but did not participate in Phase II. The TECHNIP UMBILICALS contribution escalated considerably in Phase III. Of the total \$3.4 M award, twenty percent is provided by Cost-Share Partners: Shell, Total, Baker Hughes, Weatherford, CurTran, and Technip Umbilicals. The governance of the project is described in Cost-Share Partner Agreements. Essentially, the Project Champion and the cost-share partners voted to make the end-of-phase go/no go decisions. A simple majority was required to proceed to the next phase. The team achieved both the Phases I and II product deliverables. Excellent suggestions were provided by the Cost-Share Partners who were stewards for the project.

The purpose of the project was to develop a unique carbon-based conductor for use in subsea umbilicals and power transmission in harsh marine environments. We anticipated the formation of a wire comprised of carbon nanotubes (CNT) to replace conventional copper cable. The benefits include a) weight savings, b) improved mechanical performance, and c) corrosion prevention. The decreased weight, a sixth of copper, decreases the linear mass density of an umbilical. This allows ships to carry longer umbilicals to deeper and more remote oil and gas plays, enabling greater tie back distances. The decreased weight and improved strength allows for greater top tension on the umbilicals. This opens up several possibilities, including less armoring. This also provides additional linear mass density decreases. The same conductivity as copper at reduced weight is our primary development metric; however, technologies exist in the oil and gas industry where lead is used to protect copper from corrosion. These heavy and arduous steps are not expected to be necessary with a carbon nanotube wire/cable.

The Phase III deliverable was a carbon nanotube conductor with $10^{-6} \Omega \cdot \text{cm}$ resistivity capable of operation at 37.92 MPa (5500 pounds per square inch gauge). This report documents the effort to achieve this objective as well as provides Phases I and II conclusions. For simplicity, we divide the experimental methods (**Section 2.3**) according to the tasks defined in the Project Management Plan. There are eight tasks discussed in this section. **Section 2.4 Results and Discussions** summarizes the results of the work performed during Phase III. Included with the results are recommendations to improve the technology and wire performance. The Phase III highlights include wire growth and spinning optimization, establishment of a continuous collection process, development of post-processing protocols to improve wire resistivity, and evidence of a wire with $6.7 \times 10^{-6} \Omega \cdot \text{cm}$ resistivity. Also highlighted is the performance of a pressure test on a jacketed wire. The highest pressure was 37.92 MPa.

This document also contains **Sections 2.5 Conclusions** and **2.6 Recommendations**. We recommend the continuation of the carbon nanotube wire development. The goals of the development are revised based on current status of the technology and production volume.

2. REPORT DETAILS

This section summarizes Phases I and II, as well as describes and documents the Phase III experimental methods and results.

2.1 PHASE I CONCLUSIONS

In Phase I, the NanoRidge team was successful in meeting the first year objective¹. Four wire samples with $10^{-5} \Omega \cdot \text{cm}$ electrical resistivity (deliverable) were produced, tested, and documented. In Year 1, the wire diameters and lengths were considerably larger as compared to the first laboratory scale wires reported in Nature Scientific Reports². The research team consisted of NanoRidge, Professor Barrera at Rice University with consultation from Professor Alan Windle from Cambridge University³. The following items are highlights from Phase I:

- A lab scale production furnace was situated at NanoRidge and outfitted for continuous wire formation. At the end of the year, the furnace was placed in a vertical configuration (Figure 1).
- Several improvements were made to the resistance measurement equipment (four-point probe). This was to ensure accuracy in the measurements and allow for measurements at elevated temperature and pressure.
- The wires were analyzed, and purification techniques were developed to remove the specific wire impurities. These included amorphous carbon and residual catalyst.
- Methods to reduce purification time were identified.



Figure 1. Image of the growth furnace in the vertical configuration

2.2 PHASE II CONCLUSIONS

In Phase II, the deliverable was proof of a conductor with $10^{-5} \Omega \cdot \text{cm}$ resistivity operational at 5500 psig (37.92 MPa)⁴. The team demonstrated this with five wire samples. In all cases, the resistance decreased as the pressure increased. This was attributed to the collapse of microvoids in the wire specimens. The technical team consisted of NanoRidge, Professor Barrera at Rice University with consultation from Professor Alan Windle at Cambridge University and Dave Madden at Technip Umbilicals. The items below are highlights from Phase II:

- Optimization of carbon nanotube growth provided a cleaner product.
- Several furnace subsystems were upgraded. This enabled product optimization and convenient wire collection. **Figure 2** shows the furnace process flow diagram (PFD).
- Polymer jacketing protocols were developed to over jacket the bare conductor with HDPE.
- Wire purification and doping studies were completed.
- A thorough study of the effect of pressure on resistance was performed.

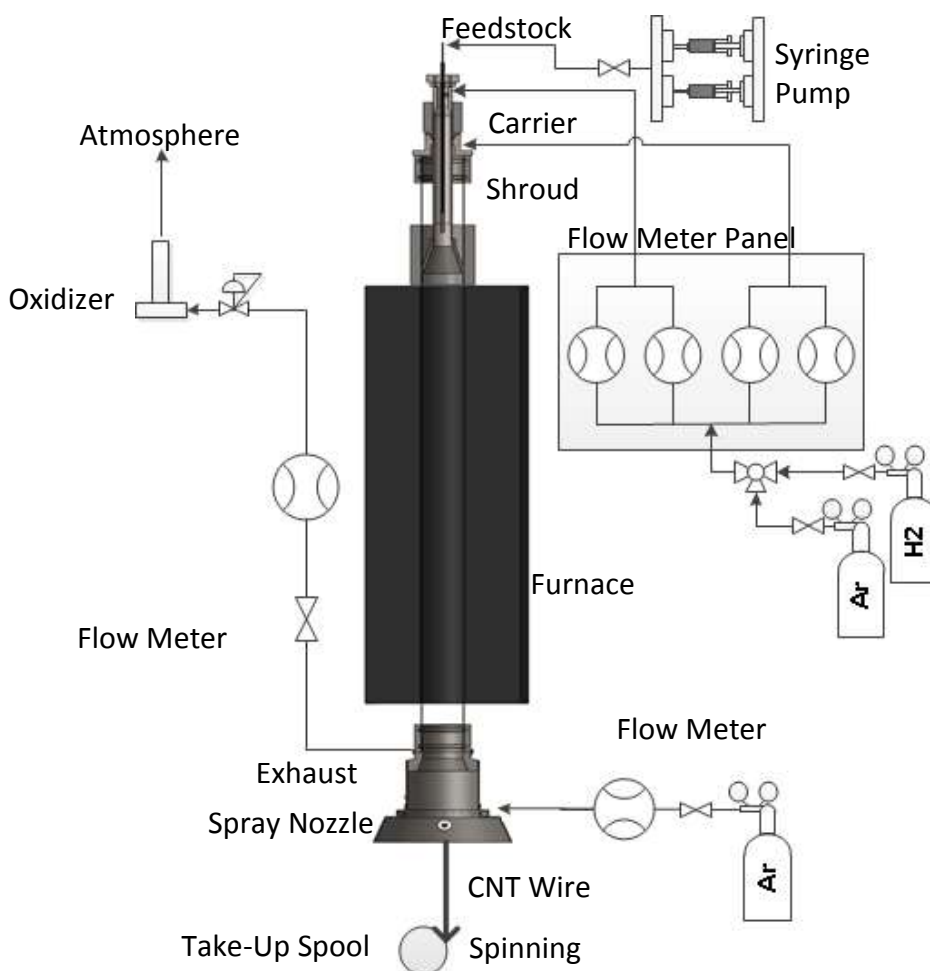


Figure 2. Process flow diagram of the Phase II furnace configuration

2.3 PHASE III EXPERIMENTAL PROGRAM

The Phase III defined goals were a) to produce a conductor with $10^{-6} \Omega \cdot \text{cm}$ resistivity operational at 5500 psig (37.92 MPa), b) manufacture the conductor to provide large diameter cable, and c) perform a demonstration program with highly conductive cable at Technip Umbilicals. The Work Breakdown Structure (WBS) in Figure 3 summarizes the tasks planned to satisfy these goals. In this section, the experimental methods, materials, and equipment used to complete the tasks are described.

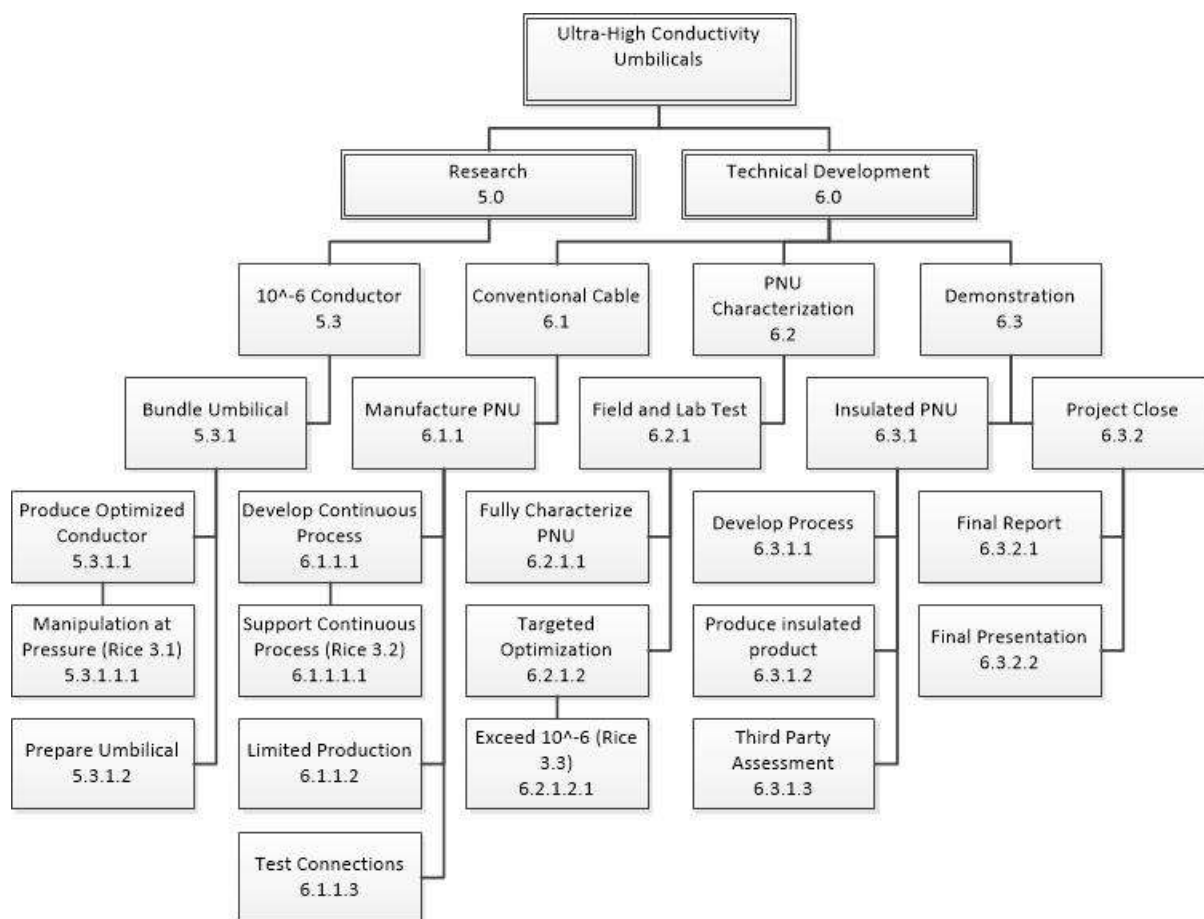


Figure 3. Tree-structure view of the WBS

This section is divided into the following subtasks:

- 2.3.1. Subtask 5.3.1.1 — Produce Optimized Conductor
- 2.3.2. Subtask 5.3.1.1.1 (Rice 3.1) — Manipulation at pressure
- 2.3.3. Subtask 6.1.1.1 — Develop Continuous Process
- 2.3.4. Subtask 6.1.1.1.1 (Rice 3.2) — Support Continuous Process
- 2.3.5. Subtask 6.1.1.2 — Limited Production
- 2.3.6. Subtask 6.1.1.3 — Test Connections
- 2.3.7. Subtask 6.2.1.2 — Targeted Optimization
- 2.3.8. Subtask 6.2.1.2.1 (Rice 3.3) — Exceed $10^{-6} \Omega \cdot \text{cm}$ resistivity

Each task is discussed separately below.

2.3.1 SUBTASK 5.3.1.1 – PRODUCE OPTIMIZED CONDUCTOR

The ideal conductor is comprised primarily of small diameter CNT with limited amounts of amorphous carbon and residual catalyst. The work in subtask 5.3.1.1 was to optimize growth to form an ideal bare conductor. The furnace from Phase II had a maximum safe operating temperature of 1150 °C. We attempted to operate at 1200 °C, but the heaters failed. Optimization performed at a growth temperature of 1150 °C gave two types of wire. The first type was comprised of the targeted small diameter CNT but was contaminated with approximately 25 to 30 weight percent of amorphous carbon, residual catalyst. The other type was relatively pure, but was comprised of large diameter CNT. This phenomenon was largely attributed to flow rate and low growth temperature. Neither of these wire types provided resistivity less than $10^{-4} \Omega \cdot \text{cm}$. After a considerable number of parameter adjustments and production runs, we concluded growth at 1150 °C would not provide the ideal conductor. As we considered the growth zone length and received input from consultants, we determined a higher temperature and longer furnace was required to satisfy this task and the goals of the project. The increased length provides increased residence time. This improves carbon efficiency and reduces the amount of residual catalyst.

In Phase III, we procured a furnace capable of operation at 1350 °C with a 48 inch, three zone heated section. Although the zones may operate independently with their own set point temperatures, we set the three zones to the same temperature. In addition, several subsystem upgrades were added to improve growth and wire uptake. One of the upgrades was the inlet flange configuration. The current inlet configuration is pictured in **Figure 4**. It has three process gas lines (inlet, carrier, and shroud) with five entrance ports. The carrier and shroud have two ports each; these are diametrically opposed for gas flow normalization. The flows of these three lines are controlled independently. This new feature enabled us to control the geometry and size of the aerogel. The carbon nanotubes grow as a low bulk density cylinder comprised of CNT and gas. This is termed an aerogel. If the cylinder is too large, it has a tendency to collect on the production tube and clog the system. If the aerogel cylinder is too narrow, the carbon conversion is low. We control the geometry by adjusting the flowrates of the three gases. At the point of feedstock introduction, we try to create chaotic flow. This gives consistent catalyst diameters within a narrow range of sizes. After the catalyst is formed and chelated with the promoter, laminar flow is necessary to provide an aerogel cylinder. This inhibits production tube clogging. We additionally considered the feedstock composition, feedstock flow rate, and furnace temperature. These results are described in **Section 2.4.1**.

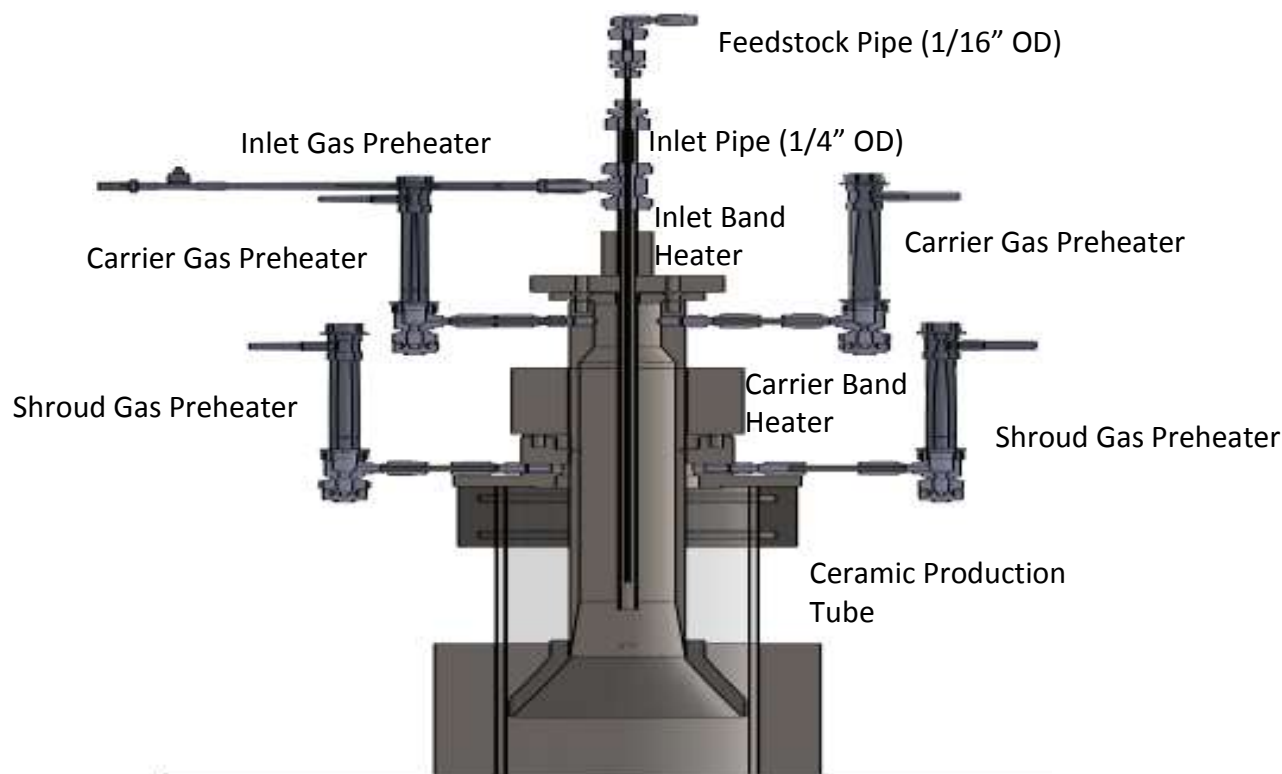


Figure 4. The Phase III inlet to furnace configuration

2.3.2 SUBTASK 5.3.1.1.1 (RICE 3.1) – MANIPULATION AT PRESSURE

Pressure tests were performed on a variety of conductors. In all laboratory tests the resistance decreased as the pressure increased. This was attributed to wire densification. The wire resistance was determined under pressure using a laboratory-scale press and a four point probe. Several nanotube wires achieved $10^{-5} \Omega \cdot \text{cm}$ resistivity at 37.92 MPa (5500 psig) pressure. The pressure tests were conducted using two methods. In method 1, the nanotube wire and the four points of connection to the probe were under pressure. This method determined the effect of pressure on the nanotube wire and nanotube-metal connections. In method 2, only the nanotube wire was pressed but not the nanotube-metal connection. This test method targeted the effect of pressure on the nanotube wire only. Both test methods provided useful data to evaluate the effect of pressure on the nanotube wire. The results of these methods can be found in the Phase II report.

Ultimately, the goal was to perform a pressure test on a jacketed wire with the pressure chamber at Technip Umbilicals. Several jacketing materials were explored at Rice. These include medium density polyethylene (MDPE), high density polyethylene (HDPE), isotactic polypropylene (PP), and amorphous polypropylene. These jacketing materials were explored by melting the polymer and dip coating the wire. The amorphous PP had the most potential. It wetted the carbon nanotube wire and demonstrated abrasion resistance and flexibility. The dip coating process did not provide a uniform coating with the selected polymers.

To improve uniformity of the coating and streamline the process, a twin screw extruder was employed. The jacketing strategy we currently pursue includes tethering the CNT wire to a

synthetic monofilament and overjacketing the mated material with HDPE. The machine used to perform the jacketing is a Lab Tech Engineering Company LTD 16 mm twin-screw extruder. This is shown in **Figure 5**. The screw barrel has 10 heated zones, a pressure transducer, 5 melt temperature controllers, and a water bath. The pelletizer was removed, as the product is collected on a take-up spool. Modifications to the system include the additions of 1) a cross-head die, 2) a pay-out system for the CNT fiber, 3) a jacketed wire take-up system, and 4) guide system. With input from Technip Umbilicals, the team decided the best jacketing material at the time was high density polyethylene (HDPE), as opposed to cross-linked polyethylene (XLPE). Both polymer materials are commonly used in subsea umbilicals. Review of ASTM D1248-12, “Standard Specification for Polyethylene Plastics Extrusion Materials for Wire and Cable” allowed the team to make material selections based on type (Type IV, $\rho > 0.96$ g/mL) and class (Class A, natural color only). This system and protocol was used to jacket a four meter CNT conductor for pressure tests at Technip Umbilicals.



Figure 5. Twin-screw extruder from Lab Tech Engineering Company LTD.

2.3.3 SUBTASK 6.1.1.1 – DEVELOP CONTINUOUS PROCESS

As the carbon nanotube growth process improved and wire take-up lengths increased, we added subsystems to enable continuous collection of the carbon nanotube conductor. The current furnace configuration is shown in **Figure 6**. One upgrade was the feedstock delivery system. We observed that our syringe pumps were slightly inconsistent, and we were limited to a 10 mL volume. We therefore added a HPLC two-piston pump with damping. The effect was obvious. This provided consistent feedstock delivery without pulsing. The resultant wire

became uniform throughout the length. Moreover, the feedstock reservoir volume can be scaled as needed for continuous operation. The reservoir is not pictured in the furnace PFD.

The second upgraded subsystem was the wire densification equipment. The number of spray nozzles was increased from three to four. As the volume in the container decreased, the pressure at the spray nozzle exit orifice decreased. This caused variability in the densification process and wire positioning. A constant volume container was added with a float sensor. A second pump was included to replenish the vessel during operation. We currently use a 55 gallon drum as the storage vessel. There is no limit to vessel size as length of production runs increase. Upgrades to a third subsystem, the take-up equipment, are discussed in **Section 2.3.5**.

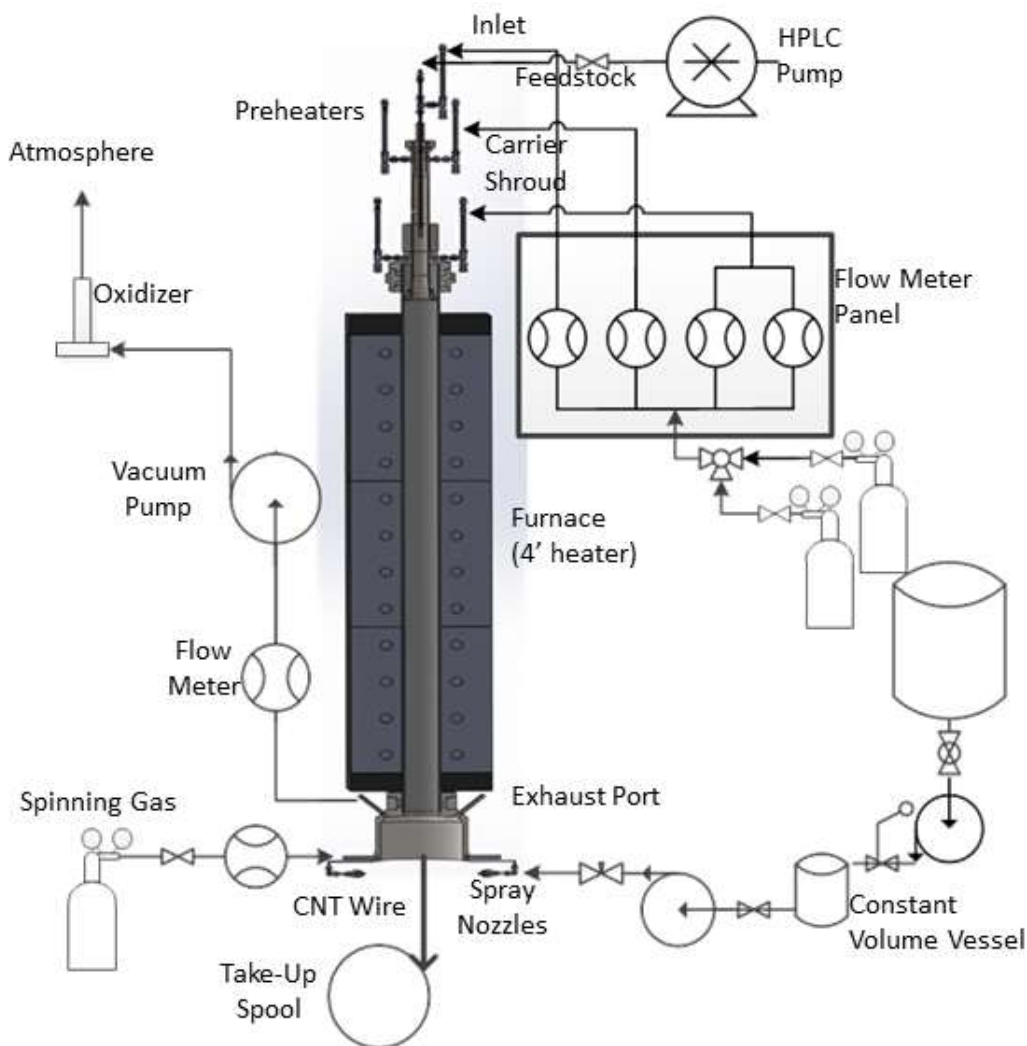


Figure 6. Current furnace configuration

2.3.4 SUBTASK 6.1.1.1.1 (RICE 3.2) – SUPPORT CONTINUOUS PROCESS

The Rice team supported the continuous wire collection work with characterization and sample testing. The mechanical, chemical, and electrical properties of carbon nanotubes have been rigorously investigated. In this arena, tremendous progress has been made in the last decade. Carbon nanotube performance decreases as the amount of defects increase. Defects cause a)

diminished mechanical strength, b) reduced optical activity, and c) increased electrical resistance. Correlation between diminished properties and different defect types is yet to be established. We anticipate optimized growth will provide a minimum of defects. Along with optimized growth, the characterization of defects was considered in the third year. Optimal conductivity can be achieved as defects in the conductors are eliminated. Defects were analyzed, and in turn, feedback was provided to NanoRidge team to support the continuous process development. Several analysis techniques were utilized; they include Raman spectroscopy (Raman), energy-dispersive x-ray spectroscopy (EDX), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). These characterization tools are briefly described below:

Raman. The Raman data provides information about G (graphitic carbon) and D (disorder) modes, G/D ratio, radial breathing modes (RBM), and fluorescence. A higher G, lower D, and less or no fluorescence are all expected results of high quality CNT. A higher D peak indicates increased defects in the wire, and any fluorescence will be due to impurities. The presence of two prominent peaks in RBM is indicative of a double-walled nanotube (DWNT) specimen. DWNT is a carbon nanotube within a nanotube. The double wall provides the system with defect tolerance giving less electron scatter. This leads to a reduction in wire resistance.

Energy Dispersive X-Ray Spectroscopy. The atomic percent and distribution of elements along the fiber length can be quantified with EDX. Some of the impurities normally encountered include sulfur and iron. The analysis is performed on sample wires at locations along its length. Wire comprised of 5 to 7 atomic percent Iron (Fe) are typical. This analysis technique aids in the chemical purification process as it indicates removal of iron.

Scanning Electron Microscopy. Images obtained by SEM provide information about the wire microscale properties, including alignment, packing efficiency, and the presence of iron and amorphous carbon impurities. CNTs aligned in the fiber direction closely packed have improved conductivity. This is due to minimization of the void space and decreased d-spacing. If the packing of nanofibers is loose, then densification of the wire or application of pressure is expected to improve conductivity. Removal of impurities, including amorphous carbon and iron, leads to improved conductivity. This is due to removal of sources of a) electron scatter and b) contact resistance. Pure samples show increases in density as well.

A large number of iron particles can sometimes contaminate the wires. This depends on the feedstock catalyst concentration. The amount and size of the catalytic nanoparticles are estimated from the SEM images. These impurities increase wire resistance also. Adjustment of the catalyst concentration in the feedstock may reduce these impurities. SEM and EDX analysis serves to determine the amount of iron contamination and aids in growth.

Thermogravimetric Analysis. Weight percent of amorphous carbon, carbon nanotubes, and residual catalyst are determined by TGA. This is a good technique to assess purity of wire. The experiments are easily prepared and experiment time is reasonable. TGA combined with EDX is a powerful wire assessment technique. TGA provides amorphous carbon weight percent, since EDX cannot distinguish types of carbon. EDX provides metal weight percent at precise locations. TGA provides the bulk metal weight percent value.

2.3.5 SUBTASK 6.1.1.2 – LIMITED PRODUCTION

To perform limited wire production, the take-up system was modified. The goal was to collect a specific number of filaments and twist these to form a cable of sufficient length to perform pressure testing and advanced electrical testing. We designed and fabricated a new take-up system. This included a motor for rotary motion of the spool and another motor to control the linear motion and position of the spool. The diameter of the spool was increased from 1.5 inches to 12 inches. This spool gave a twisted wire length of 37.7 inches. The 3-foot wire specimen was ideal for electrical testing and characterization. To perform initial pressure tests at Technip Umbilicals, the 12 inch spool was replaced with a 42 inch diameter spool. This provided wires 3.3 meters in length. The as-produced twisted wire was analyzed and then jacketed. The HDPE jacketed wire was subjected to a pressure test at Technip Umbilicals. We fabricated an additional spool with a diameter of 123 inches. This shall provide a wire close to 10 meters long. The spool was not used to collect wire, however, as the project came to a close before installation.

2.3.6 SUBTASK 6.1.1.3 – TEST CONNECTIONS

A variety of connections were formed to determine if new terminations were required or if standard copper terminations would suffice. The connections are listed below:

- The resistance of a wire was recorded. The wire was cut in half. The two wire segments were butt spliced with standard electrical splices. The resistance was determined to be the same with the splice.
- Two jacketed wires were used to form an extension cord. The ends were terminated with plugs with screw terminals. There was no difference in resistance when measured at the bare ends or the plug terminals.
- Our standard four-point probe testing protocol has copper pads that compress the wire at an exact location. We do not see changes in resistance when a silver paste is used for the measurement. We report the results from the standard testing protocol.
- Since the jacketed wire tested at Technip Umbilicals was shorter than the length of the chamber (6 meters), the wire was spliced with copper using silver paste and a potting compound. The splice or connection remained intact, although the resistance changed slightly. The resistance range was 151 to 154 Ω .

These were observations recorded during the project. A more thorough study of connector options is anticipated as the technology matures. We recommend thorough testing of a product specific terminator

2.3.7 SUBTASK 6.2.1.2 – TARGETED OPTIMIZATION

Several areas were considered for optimization. Optimization of carbon nanotube growth entails selection of the proper feedstock flow rate, gas flow rates, preheat temperature settings, and furnace temperature. These constitute a considerable number of variables. The result of optimized growth is a carbon nanotube wire with 1) a limited amount of contamination, 2) good CNT alignment in the fiber direction, and 3) a relatively dense and

strong as-produced material⁵. We focused on feedstock composition, feedstock flow rate, and production temperatures. Other optimization areas include:

- **Densification.** This process is not well defined at this time, but densification is critical to improve the electrical and mechanical wire performance. The pressure study indicates efficacy in this area.
- **Purification.** This was an area of focus during this project. There is a balance between purification and carbon nanotube degradation. An optimum is required as this becomes a post-processing in-line production step. Purification residence times are determined by the output rate, purification efficiency, and size of vessel. A thorough study would define these variables
- **Doping.** We demonstrated an order of magnitude improvement to resistivity with iodine doping. Iodine doping performed while monitoring the resistance is an optimization step.

Growth optimization results are discussed in **Section 2.4.1**.

2.3.8 SUBTASK 6.2.1.2.1 (RICE 3.3) – EXCEED $10^{-6} \Omega \cdot \text{cm}$ RESISTIVITY

The mechanisms of carbon nanotube electrical conduction are distinct from metals, such as copper or aluminum. For nanotubes, two mechanisms dominate. The first mode is ballistic transport⁶. Electrons move practically uninhibited along the nanotube surface. This is the case for defect free, uncontaminated carbon nanotubes. The second mode is resonant quantum tunneling⁷. Here electrons move from one nanotube to the next. The resistivity is determined by inter-nanotube spacing, defects, and contamination. To minimize resistance in this mode requires wire purity, densification, and carbon nanotube alignment. Additional improvements may be made by purification and doping.

A nanowire comprised of 95 to 98 percent carbon nanotubes subjected to drawing and densification is expected to provide exceptional conductivity. We expect this type of wire to equal or exceed the conductivity of copper. Copper has a resistivity of $1.7 \times 10^{-6} \Omega \cdot \text{cm}$. To exceed this resistivity, contact resistance must be held to a minimum. Two main causes of contact resistance in a highly conductive wire are void space and carbon nanotube interconnects⁸. The void space is diminished by drawing and densification but will never be completely removed. A solution for both forms of contact resistance is intercalation of charge carriers⁹. Iodine doping was explored during this project. Figure 7 shows aligned carbon nanotubes with intercalated iodine molecules. This structure would certainly have lower resistance than a wire with a considerable number of voids.

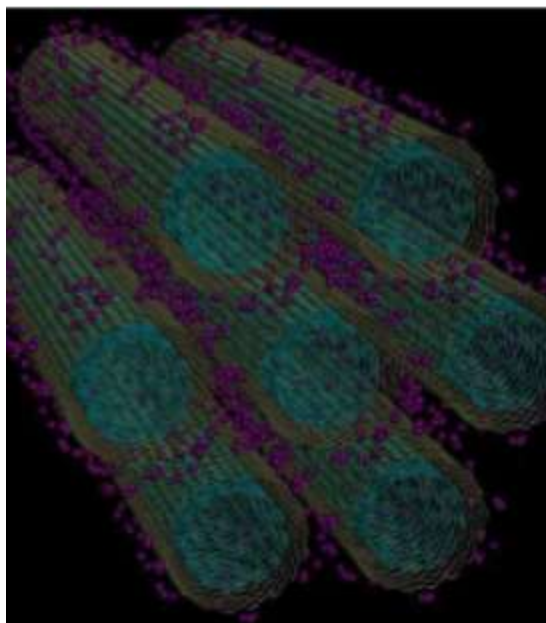


Figure 7. Iodine molecules distributed on DWNT

In addition to iodine doping investigations, pressure testing was performed. Pressure serves as a densification step. Densification is considered indispensable in the formation of highly conductive carbon nanotube wires. The results are discussed in **Section 2.4**.

2.4 PHASE III RESULTS AND RECOMMENDATIONS

This section describes the results obtained in Phase III.

2.4.1 GROWTH OPTIMIZATION

Several parameters were adjusted during the course of growth optimization. The first parameter was the **feedstock composition**. This parameter study was performed on the 1150 °C furnace and extended to the 1350 °C furnace. The feedstock was a ternary mixture composed of a catalyst precursor, promoter, and carbon source. The catalyst precursor and carbon source was not changed. The weight percent ratio of the mixture was altered, and two promoters were investigated. Approximately 200 experiments were performed. The material was collected in wire form and characterized by thermogravimetric analysis (TGA) and four point probe resistivity. Several trends were observed; they are listed below:

- As the catalyst precursor concentration increases, the residual catalyst concentration in the wire increases.
- A promoter with a low decomposition temperature is ideal as the promoter inhibits the growth of large catalyst particles. The promoter serves two roles. It inhibits the catalyst from growing larger and aids in carbon decomposition and carbon solubility. The sooner the promoter is made available, the smaller the diameter of the carbon nanotubes. The promoter is made available to the catalyst once the promoter decomposition temperature is reached.

- There is an ideal promoter percent based on the catalyst precursor. The promoter active atom should be in slight excess compared to the catalyst precursor active atom. Neither starving the system of promoter nor adding a large excess of promoter provides a spinnable material. A material is spinnable if the carbon nanotubes have a high van der Waals attraction, and form a cylinder as a result of laminar flow.

Recommendation. Feedstock optimization was performed until the wire had a minimum of residual catalyst and the system was reproducibly spinnable. A design of an experimental approach would be useful to find the feedstock composition optimum.

The second parameter explored was the **feedstock flow rate**. The optimum flow rate changes with furnace temperature. Nevertheless, too high of a flow rate gives poor growth and high metal content in the nanowire. When the feedstock flow rate is too low, the bulk density of the aerogel is diminished. This gives a small diameter wire that is not easily collected. As the furnace temperature increases the feedstock flow rate decreases.

Recommendation. The trends we observed were anticipated; however, the feedstock flow rate optimum depends on mass flow, bulk density, and temperature gradient. A modeling and simulation effort would be greatly beneficial to calculate the optimum feedstock flow rate and extrapolate the results for a larger diameter production tube.

The third and final parameter we considered was **furnace temperature**. As mentioned, growth at 1150 °C would not provide the quality of wire required for this project. Once the 1350 °C furnace was installed, growth at elevated temperature was investigated. We observed increases in growth rate and carbon nanotube density as the temperature increased. Adjustment of the feedstock flow rate was required to prevent production tube clogging. Since the growth rate is increased, the residual catalyst in the wire is decreased as the furnace temperature is increased. Experiments were performed to find an optimum feedstock flow rate at 1350 °C. The wire collected at 1350 °C with an optimized feedstock composition and flow rate is approaching the wire purity requirements (Figure 8). For example, sample NR3222 is comprised of 90 percent carbon nanotube carbon. The residual catalyst is at a minimum, and the primary contamination is amorphous carbon, which is less challenging to remove than residual catalyst.

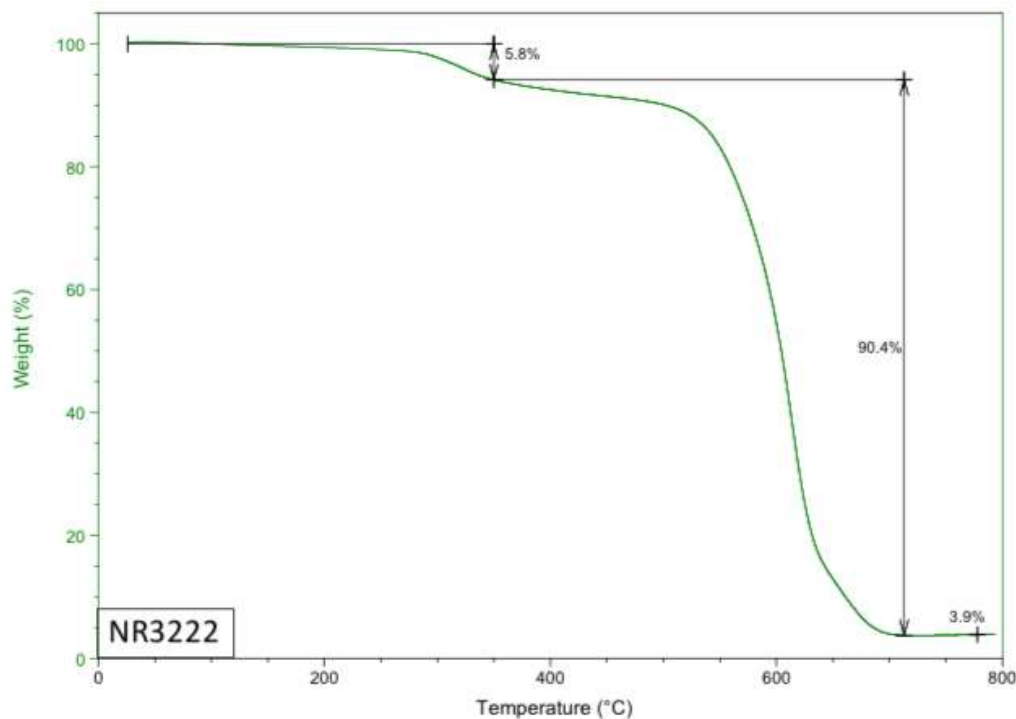


Figure 8. TGA of sample NR 3222

Recommendation. Wires with the level of purity of sample NR3222 were collected at the end of Phase III. With additional time, resources, and comprehensive development work, further improvements will be achieved.

2.4.2 CONTINUOUS PRODUCTION

As discussed previously, several upgrades were made to the wire collection subsystems. The results are summarized in this section. Carbon nanotube growth is a principle factor for continuous production. The aerogel is easily controlled with gas flow rate adjustment when the growth is optimized. The second factor is the precise position and pressure of the organic spray nozzles. The four nozzles enabled centering of the aerogel and wire. The third factor is synchronization of carbon nanotube growth with wire collection. If collection is too slow, the carbon nanotubes clog the production tube. If collection is too fast, the material is removed faster than formed and does not remain continuous. We explored these parameters until a continuous set of conditions were determined. Our longest continuous run was four hours. This translates into 1.44 kilometers of continuous carbon nanotube wire. This was performed twice and collected on the 42-inch diameter spool. It yielded a 3.3 meter, 28 AWG wire with an as-produced resistivity of $5.7 \times 10^{-4} \Omega \cdot \text{cm}$. This wire was jacketed without post-processing and subjected to a pressure test.

Recommendation. Continuous collection of carbon nanotube wire was demonstrated. The filament diameters are between 0.012 and 0.04 mm. The wire diameter scales with the production tube diameter. Simulation and calculation will provide the production tube diameter required to directly form a 28 AWG carbon nanotube filament. An optimized wire with this diameter would satisfy multiple product opportunities.

2.4.3 WIRE CHARACTERIZATION AND PURIFICATION

Raman spectroscopy was performed at Rice University by the Rice team to characterize the carbon nanotube wires that had been formed at NanoRidge. **Figure 9** illustrates the efficacy of Raman analysis. NR030215B3 was analyzed before and after purification. Both spectra are indicative of small diameter carbon nanotubes (RBM) with limited defects (small D peak). The RBM region (**Figure 10**) of the purified wire (red line) clearly indicates DWNT. With the as-produced material (black line), the RBM region is masked somewhat by contamination. Multiple samples were analyzed by Raman before and after purification. Sample NR031215B3 is a good example of expected analysis, purification outcomes.

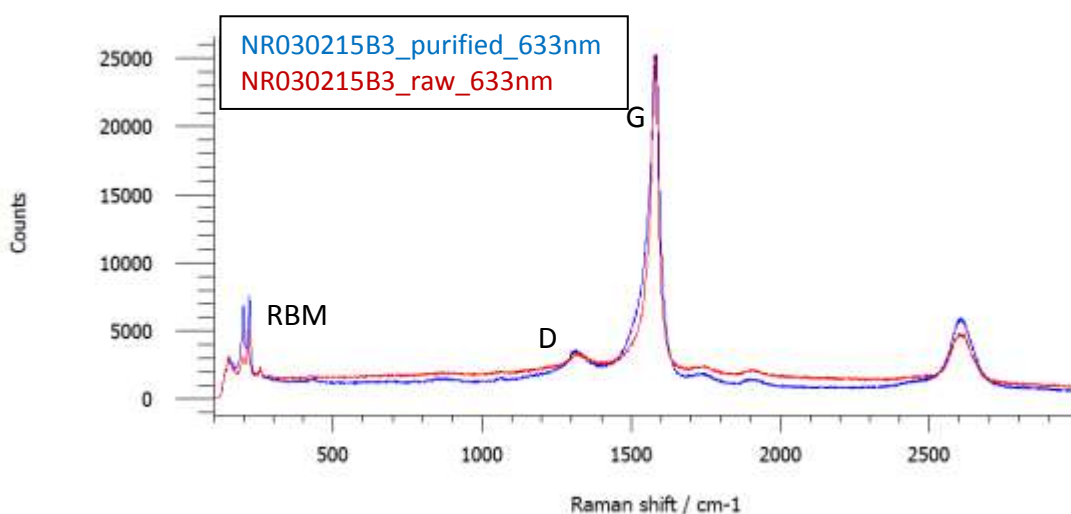


Figure 9. Full Raman spectra of NR031215B3 before and after purification

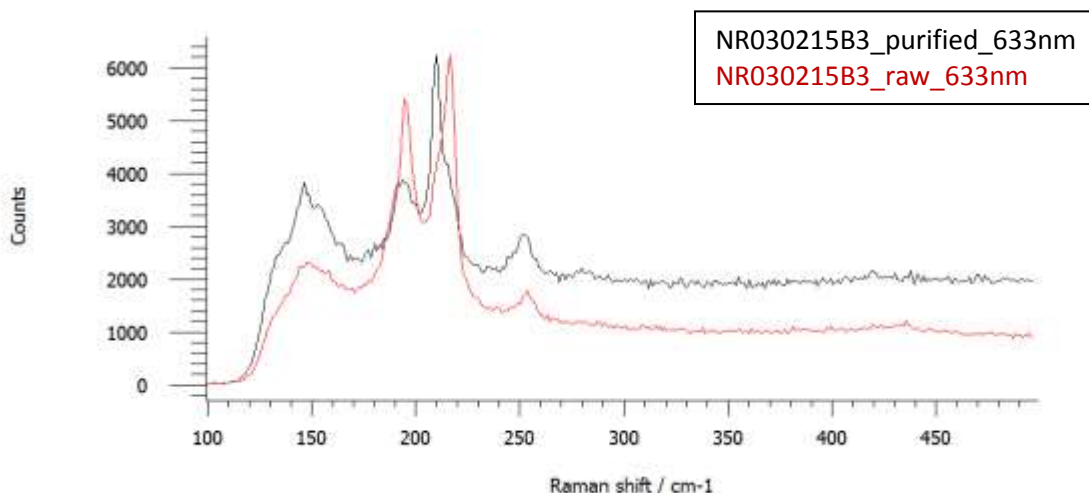


Figure 10. RBM region of NR031215B3 before and after purification

The carbon nanotube wires with good resistivity and correct Raman spectrum were further analyzed by SEM and EDX. These two characterization techniques are performed on the same instrument. Wire sample NR111914B4 was a good example of the assessment of purification by SEM/EDX. **Figure 11** shows SEM micrographs of the as-produced wire. The 50,000X magnification image shows small diameter CNT with amorphous carbon contamination. The brighter nodules are amorphous carbon. The EDX analysis (**Figure 12**) indicates a carbon-to-iron weight ratio of 85:15. This is a large residual metal percent.

Heated hydrochloric acid is used in a purification technique that targets the removal of metals from carbon nanotube samples. The purification was performed and the wire was reassessed by SEM/EDX. **Figure 13** shows the SEM micrographs of the purified wire. The 50,000X magnification image indicates the presence of amorphous carbon. The purification targeted metal that was not amorphous carbon. The EDX analysis (**Figure 14**) of the purified wire indicates a 50 percent metal reduction. The use of SEM/EDX in combination with TGA is an excellent combination of characterization techniques to determine variety of impurities and track purification protocols.

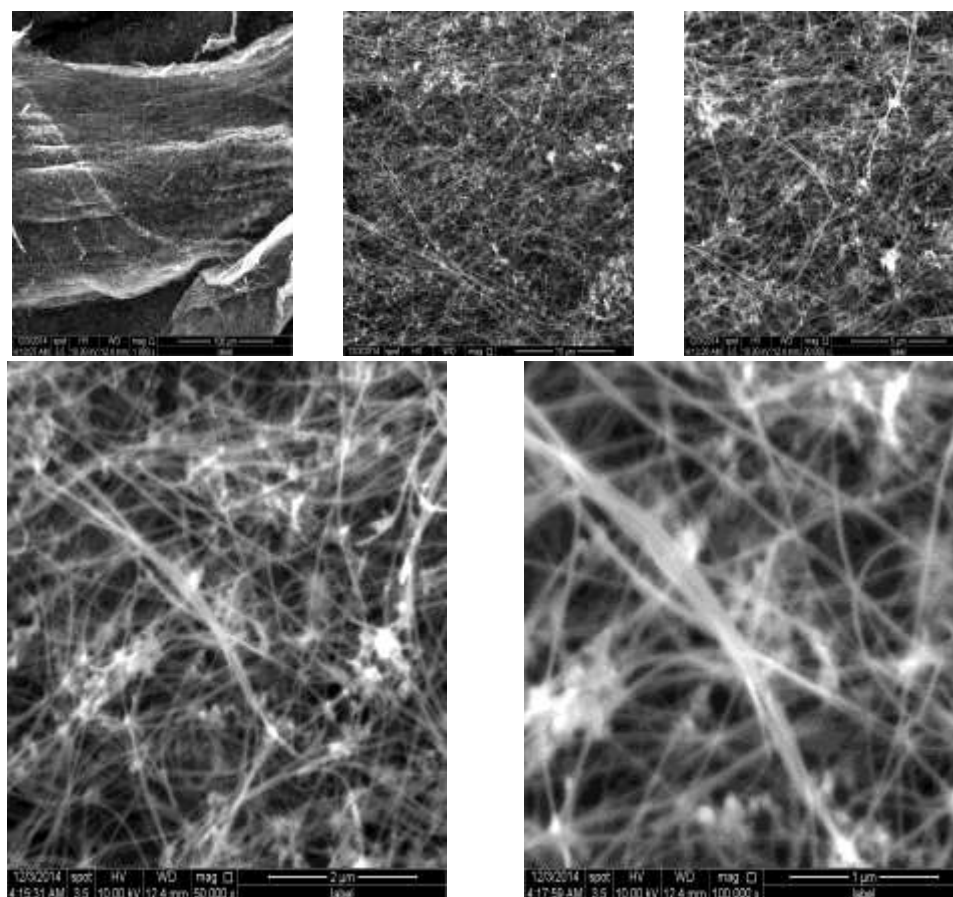


Figure 11. SEM micrographs of as-produced NR111914B4

NR111914B4
 EDX Results
 Raw

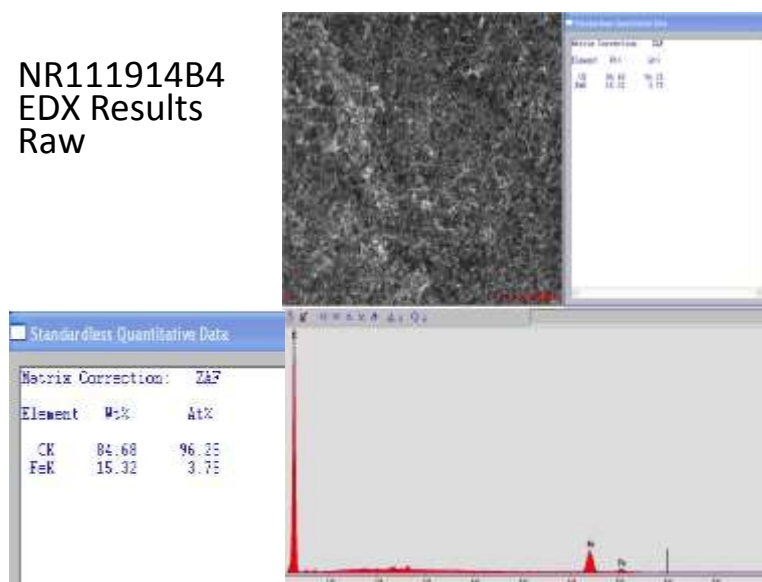


Figure 12. EDX elemental analysis of as-produced NR111914B4

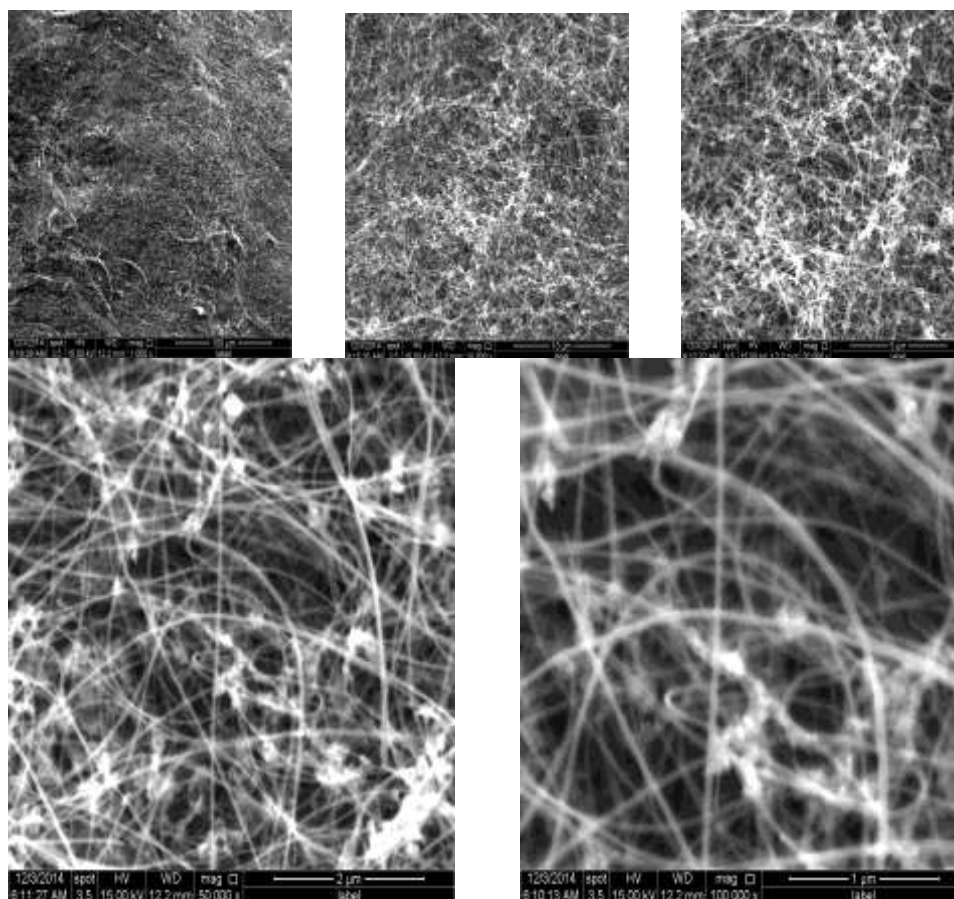


Figure 13. SEM micrographs of NR111914B4 treated hot HCl

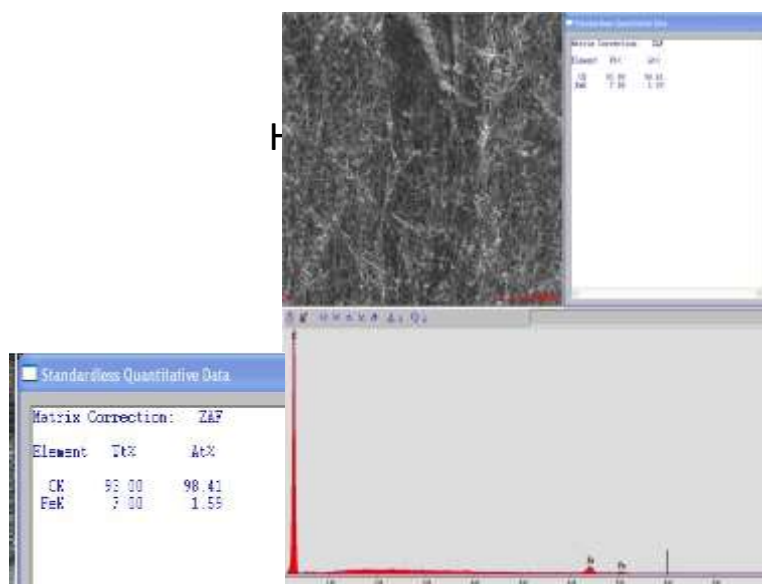


Figure 14. EDX elemental analysis of HCl treated NR111914B4

In conclusion, several characterization techniques were applied to determine the composition of wires and to select proper purification techniques. Purification methods were developed to

target the removal of specific contamination sources. One method was developed to remove amorphous carbon, and a second method was developed to remove residual metal. During the project, we determined the effect of purification on wire resistivity. This is discussed in the next section.

2.4.4 ELECTRICAL AND PRESSURE TESTING RESULTS

As the wire take-up system matured, four-point probe resistivity measurements were performed on all the carbon nanotube wires. We focused on resistivity reduction throughout the course of the project. The resistivity went from approximately $1.5 \times 10^{-3} \Omega \cdot \text{cm}$ to the lowest of $5.7 \times 10^{-4} \Omega \cdot \text{cm}$ as we optimized growth and obtained cleaner wires. This was important to demonstrate, as carbon fiber has a resistivity of $1.5 \times 10^{-3} \Omega \cdot \text{cm}$. Carbon fiber is essentially dense folded graphite in fiber form. However, resistivity of $10^{-4} \Omega \cdot \text{cm}$ is lower than graphite wire. We expect to form as-produced wire with a resistivity of $10^{-5} \Omega \cdot \text{cm}$ in due course. With this level of as-produced resistivity, $10^{-6} \Omega \cdot \text{cm}$ is comfortably achievable by post-processing.

The technical team developed protocols to improve the resistivity to $10^{-5} \Omega \cdot \text{cm}$, some of which are highlighted in **Table 1**. The first wire resistivity decrease was achieved through iodine doping. This provided a greater than order of magnitude decrease in resistivity. Wire EY092013 is an example of doping to achieve enhancement to conductivity. The second wire resistivity decrease occurred as a result of purification. Once the two-step purification technique was developed and optimized, it was employed on a number of wires. Purification gave a similar level of improvement as compared to iodine doping. Wire sample 022715B1 is an example in which the as-produced resistivity was 1.6×10^{-3} ; then, following purification, the resistivity decreased to $3.2 \times 10^{-5} \Omega \cdot \text{cm}$. This change is close to a two order of magnitude improvement. The last technique highlighted is a copper treatment protocol. Following a publication¹⁰ that reported a 100 times increase in ampacity, we coated the carbon nanotube wire with copper. The process involved a) copper doping of the wire, b) plating copper to the wire outer skin, and then c) annealing the copper in a reducing atmosphere. This provided a wire with $6.7 \times 10^{-6} \Omega \cdot \text{cm}$ resistivity. At this time, work is being conducted to reduce the as-produced wire resistivity to $10^{-5} \Omega \cdot \text{cm}$ and perform post-processing on the wire to lower the resistivity to $10^{-6} \Omega \cdot \text{cm}$. The minimal copper coating allows the carbon nanotube voids to be filled with CuO. This addresses densification concerns. Additionally, the copper coating is a minimum so the weight increase is only 10 weight percent. The load is carried by the carbon nanotube component; therefore, the copper is not subjected to tension.

Table 1. Examples of improvement of as-produced wire resistivity

Name	Treatment	Resistance (Ω)	Diameter (mm)	Resistivity ($\Omega \cdot \text{cm}$)
EY092013	As-Produced			1.3×10^{-3}
EY092013	Iodine Doping			7.9×10^{-5}
022715B1	As-Produced	34.1	0.162	1.6×10^{-3}

022715B1	Two-Step Purification	24.7	0.027	3.2×10^{-5}
020816C3	As-Produced	6.17	0.248	7.8×10^{-4}
020816C3	Copper Treatment	0.042	0.299	6.7×10^{-6}

As mentioned previously, a ten-foot wire specimen 101515C1 was jacketed with HDPE and tested to 5504 psig. **Figure 15** shows the test apparatus located at Technip Umbilicals. The carbon nanotube wire was spliced into the yellow wires. The nanowire specimen was fully immersed in the pressure chamber. After jacketing losses and failed potting attempts, the tested wire length was 24 inches. The nanowire was spliced into the copper wire by wrapping the copper with the nanowire. This was secured with silver paste. The splice was protected by potting compound. The yellow copper wire had an outer diameter of 0.2 inches and served to form a seal with the flange compression fitting. The result of the pressure test is shown in Figure 16. There was an initial decrease in resistance, followed by a slight increase. We attributed this to the splices, as pressure tests on bare nanowire show a decrease in resistance. There was not sufficient time to perform this same pressure test with a $10^{-6} \Omega \cdot \text{cm}$ resistivity jacketed nanowire. The as-produced wire 101515C1 had a resistivity of $5.7 \times 10^{-4} \Omega \cdot \text{cm}$. Once funding is secured, pressure test of full length (6 meter) NanoWire with $10^{-6} \Omega \cdot \text{cm}$ resistivity is a main priority.



Figure 15. Pressure test chamber at Technip Umbilicals

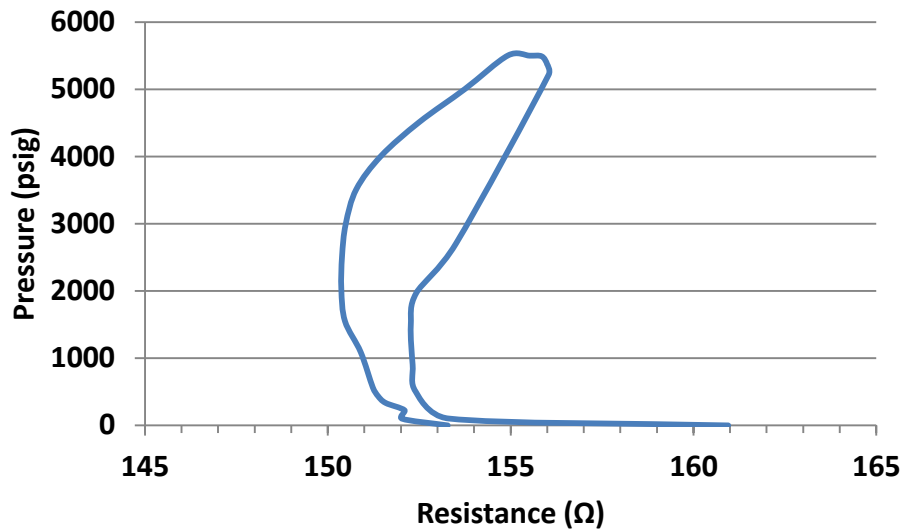


Figure 16. Pressure versus resistance of wire 101515C1

Recommendation. None of the wires were densified. This is considered critical to achieve lower resistivity. We recommend tasks and experiments to determine densification steps.

2.5 CONCLUSIONS

Work was conducted according to the Project Management Plan. The key achievements were:

- Proof of concept for continuous manufacture of the NanoWire. The elevated temperature furnace enabled optimization of the carbon nanotube growth process. This was an important achievement.
- High purity carbon nanotube growth products exceeding 90 weight percent. Results indicate 95 percent purity is expected. This gives advanced conductivity and strength.
- Techniques were developed to improve the resistivity of as-produced wires. We achieved low $10^{-5} \Omega \cdot \text{cm}$ resistivity with carbon nanotube wires. A new copper coating protocol provided a wire with $6.7 \times 10^{-6} \Omega \cdot \text{cm}$ resistivity. This is an interesting way forward, though the ultimate goal is to achieve copper resistivity with a carbon nanotube wire.
- A jacketed wire was tested at 5500 psig pressure with minor changes to the resistance.
- We identified high speed data transmission ribbon or cable as a valuable new product. Testing is required to proceed to commercialization. This will provide resources to further develop a power transmission cable.

2.6 RECOMMENDATIONS

We highly recommend continuation of the development program. Realistically, a power transmission cable comprised exclusively of carbon nanotubes would require much greater volumes and monofilament diameters. This is expected to come from a larger diameter furnace that forms a 28 AWG filament. At the current production volume, we are able to satisfy high speed data transmission wire requirements. We intend to perform high frequency electrical tests on as-produced and purified wires in the near future. We fully expect resistivity to

improve as growth is optimized at a furnace temperature of 1350 °C. Continuation of the development program is expected to provide NanoWire resistivity improvements and a high speed data transmission product in the short-term.

With a commercial product and $10^{-6} \Omega \cdot \text{cm}$ resistivity, we plan to add a larger furnace that will continuously produce a 28 AWG NanoWire product. The output from the new furnace will satisfy power transmission cable requirements. We plan to commercialize this wire and braid several of these to form a power cable umbilical prototype. From here, a production facility to form exclusively wire for umbilicals will be designed and built. The commercial product from the larger furnace is expected to take 18 months from project start. Formation of wire from the production facility will occur in Year 3. This assumes resources are readily available.

In brief we recommend the following immediate actions:

- Use process analysis and simulation to optimize furnace growth and design a scaled furnace
- Develop the business cases for data transmission, motor windings, and power transmission
- Develop plan to qualify our current wire. This lessens risk in development and increases the Technology Readiness Level from 3 to 7.

3. FIGURES AND TABLES

Below are the lists of figures and tables:

List of Figures

Figure 1. Image of the growth furnace in the vertical configuration	8
Figure 2. Process flow diagram of the Phase II furnace configuration	9
Figure 3. Tree-structure view of the WBS	10
Figure 4. The Phase III inlet configuration	12
Figure 5. Twin-screw extruder from Lab Tech Engineering Company LTD.....	13
Figure 6. Current furnace configuration	14
Figure 7. Iodine molecules distributed on DWNT.....	18
Figure 8. TGA of sample NR 3222	20
Figure 9. Full Raman spectra of NR031215B3 before and after purification	21
Figure 10. RBM region of NR031215B3 before and after purification	22
Figure 11. SEM micrographs of as-produced NR111914B4.....	23
Figure 12. EDX elemental analysis of as-produced NR111914B4.....	23
Figure 13. SEM micrographs of NR111914B4 treated hot HCl	24
Figure 14. EDX elemental analysis of HCl treated NR111914B4	24
Figure 15. Pressure test chamber at Technip Umbilicals	27
Figure 16. Pressure versus resistance of wire 101515C1	28

List of Tables

Table 1. Examples of improvement of as-produced wire resistivity	25
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5. LIST OF ACRONYMS AND ABBREVIATIONS

Below is a table listing the acronyms and abbreviations included in this document.

AWG	American Wire Gauge
CNT	Carbon Nanotubes
CVD	Chemical Vapor Deposition
D	Disorder Mode
DWNT	Double Walled Carbon Nanotubes
EDX	Energy-Dispersive X-Ray Spectroscopy
G	Tangential Mode
HDPE	High Density Polyethylene
MDPE	Medium Density Polyethylene

MPa	MegaPascal
PMP	Project Management Plan
PNU®	Polymer Nanotube Umbilical
Psig	Pounds per square inch gauge
PP	Polypropylene
RBM	Radial Breathing Mode
RPSEA	Research Partnership to Secure Energy for America
SEM	Scanning Electron Microscope
SWNT	Single Walled Carbon Nanotubes
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
UDW	Ultra-Deepwater